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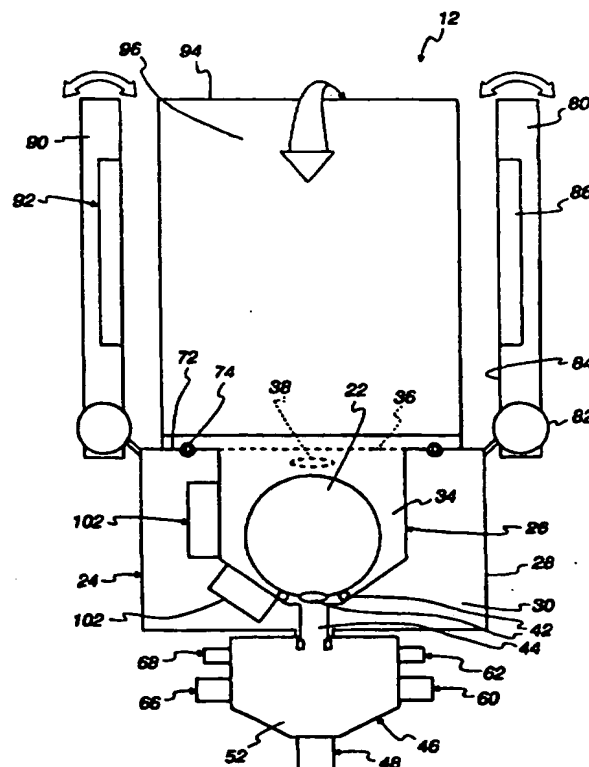
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(54) Title: METHOD AND APPARATUS FOR IMMERSION TREATMENT OF SEMICONDUCTOR AND OTHER DEVICES

(57) Abstract

Method and apparatus (10) for cleaning semiconductor devices (22) and other workpieces using an aqueous rinse solution which is deoxygenated by passing the aqueous rinse solution and a carrier gas through an osmotic membrane degasifier. A cleaning chamber (26) is also disclosed for carrying out the cleaning method.



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**METHOD AND APPARATUS FOR IMMERSION  
TREATMENT OF SEMICONDUCTOR AND OTHER DEVICES**

**BACKGROUND OF THE INVENTION**

**1. Field of the Invention:**

5           The present invention pertains to the aqueous processing of various articles, including the immersion cleaning of semiconductor wafers, using deoxygenated aqueous rinse solutions.

**2. Description of the Related Art:**

10           As will be seen herein, the present invention is directed to the aqueous treatment of a wide variety of commercially important articles, such as liquid crystal displays, flat panel displays, memory storage disk substrates, as well as photographic plates and  
15 film. The present invention has found immediate commercial acceptance in the field of semiconductor wafers, especially wafers of a type which are ultimately divided to form a plurality of electronic devices.

20           During the course of producing commercial semiconductor wafers, layers of various materials are built up on one surface of a wafer blank. These various layers are processed using several different etching techniques, each of which results in a residue  
25 which impairs further device fabrication. It is important that such residues be effectively removed. Typically, the several types of residue are removed with solvents especially adapted for the particular residues. While such solvents are generally effective  
30 for removing residues, solvents remaining on the surfaces of the semiconductor device also impair further device fabrication steps.

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Accordingly, it is important that the solvents be removed from the semiconductor device and it is known that water rinsing is an efficient means of solvent removal. However, semiconductor device layer materials have changed over the years, and presently semiconductor device manufacturers are employing materials which are subject to corrosion upon contact with water. In an effort to reduce the corrosion problem, carbon dioxide gas has been sparged, i.e., bubbled, into the rinse water to partially lower the pH of the rinse water. However, bubbling carbon dioxide into water rinses used in the semiconductor device fabrication industry has proven to be only marginally successful in reducing the extent of corrosion, and further adds the risk of introducing contaminating particles into solution. In an effort to overcome growing problems of corrosion, the semiconductor device fabrication industry has investigated intermediate rinse steps using non-aqueous rinse solutions. However, such non-aqueous solutions have proven to be less effective than rinse water in removing solvents and wafers are still routinely rinsed with water, despite the corrosion effects.

Significant efforts have been expended in reducing the amount of exposure of a wafer containing alloys of copper and aluminum to rinse water. However, it appears that, in order to meet future requirements for improved electrical performance, the aluminum content of the alloy must be substantially reduced and possibly eliminated, thus substantially increasing the susceptibility of the wafer layer materials to corrosion, at higher levels than those presently experienced.

One example of efforts to improve wafer production involves oxygen removal to reduce oxide

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growth on the surface of semiconductor wafers. For example, literature describing the PALL SEPAREL Model EFM-530 Degasification Module addresses the reduction of dissolved oxygen in deionized water, in a manner which avoids potential defects to semiconductor devices caused by the formation of unwanted oxide layers. As is known in the art, an oxide layer forms when pure silicon is exposed to an oxygen source, such as dissolved oxygen in a rinse water or other aqueous medium. The oxide layer can change the surface of the silicon from hydrophobic to hydrophilic, a condition which is undesirable in some aspects of wafer processing, such as pre-diffusion cleaning operations. Accordingly, the PALL Degasification Module addresses the need to decxygenate rinse water to avoid formation of a silicon dioxide layer in the rinse after the wafer is treated with an HF etch solution. As can be seen, the problem addressed by the PALL Degasification Module is not related to problems encountered in controlling corrosion of aluminum, such as pitting and etching, as has been experienced in processing wafers carrying copper/aluminum structures on their surface. While dissolved oxygen is also objectionable from a corrosion standpoint, the corrosion problem is not concerned with the formation of unwanted oxides. A further, more complete system control over wafer processing so as to reduce corrosion in wafers containing copper/aluminum structures is needed.

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide cleaning for semiconductor wafers using aqueous solutions which are treated in a manner to eliminate corrosion of semiconductor device materials layered on semiconductor substrates.

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Another object of the present invention is to provide cleaning of the above-described type which is effective even in relatively small, hollow structures formed in a semiconductor surface, such as vias.

5 A further object of the present invention is to provide aqueous treatment of the type described above which removes dissolved oxygen from an aqueous solution while controlling the pH of the aqueous solution.

10 Another object of the present invention is to provide arrangements for aqueous treatment of many different types of devices using conventional readily obtained equipment, and consumables which are relatively inexpensive.

15 Yet another object of the present invention is to provide process arrangements of the type described above by employing an osmotic membrane degasifier and using a carrier fluid (preferably a gas) comprised of one or more components, preferably for  
20 oxygen removal and, optionally, pH control or other chemical adjustment to the aqueous solutions.

These and other objects according to principles of the present invention are provided in apparatus for processing a workpiece, comprising:

25 a cleaning chamber defining a cavity for receiving the workpiece and a device opening through which said workpiece is passed into and out of the cavity;

an osmotic membrane degasifier defining a  
30 degasifier cavity, a membrane dividing the degasifier cavity into first and second parts, a aqueous solution inlet and a aqueous solution outlet associated with said first part to direct aqueous solution into contact with one side of the membrane, and a carrier gas inlet  
35 and a carrier gas outlet associated with said second

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part to direct carrier gas into contact with the other side of the membrane;

and the aqueous solution outlet coupled to the cleaning chamber.

5                    BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a front elevational view of cleaning apparatus according to principles of the present invention;

FIG. 2 is a schematic plan view thereof;

10                  FIG. 3 is a cross-sectional view taken along the line 3-3 of FIG. 2;

FIG. 4 is a schematic diagram thereof; and

FIGS. 5-8 show a sequence of operation.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

15                  As mentioned above, the present invention has found immediate application in the field of semiconductor device fabrication. However, in providing methods and apparatus for carrying out controlled immersion processing operations as well as providing  
20 deoxidized and/or pH-controlled aqueous solutions, the present invention is readily adaptable to a wide range of commercially significant activities, such as the photographic processing of plates, films and prints, and the fabrication of liquid crystal and flat panel  
25 displays, as well as articles requiring highly refined surface finishes, such as hard disk memory substrates. As will be seen below, the present invention will be described with reference to the processing of semiconductor wafers, although it will become readily  
30 apparent to those skilled in the art that other types of workpieces other than semiconductor wafers and immersion processing other than aqueous cleaning and/or

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rinsing of semiconductor wafers is also encompassed within the scope of the present invention.

Semiconductor wafers are typically fabricated by forming a layered series of devices integrated with an underlying semiconductor blank or so-called "prime wafer". With the formation of each layer, the wafer in process must be polished and cleaned in preparation for the next layering step. With ongoing changes in layer materials, new, challenging processing problems have arisen. In general, the unit cost of individual wafers is increasing dramatically and, accordingly, even partial losses of wafers being processed result in an expensive penalty for the wafer fabricator. Unwanted materials, such as contamination particles and residues associated with via etching or metal etching processes, can cause subsequent layering operations to fail. Such residues and contamination particles associated therewith are typically removed using various solvents. The solvents are then removed with one or more rinse solutions, and the present invention has found immediate acceptance in providing aqueous solutions (i.e., solutions whose composition is either exclusively or predominantly comprised of water) for use in such cleaning and especially in rinsing operations.

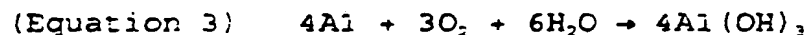
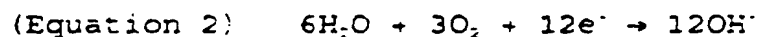
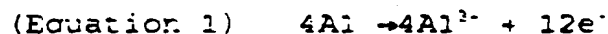
Increasing use is being made of device layer materials (such as aluminum/copper alloys and proposed all-copper structures) which have greater susceptibilities to corrosion when exposed to water rinses. However, as is widely recognized, there are strong advantages in employing aqueous solutions for wafer rinse. For example, compared to non-aqueous rinses (i.e., rinses not predominantly comprised of water), such as isopropyl alcohol (IPA) or N-methyl pyrrolidone (NMP), aqueous rinse solutions require less investment



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cost, less safety precautions, are more affordable to dispose of when their useful life has expired, and for many types of popular solvents, aqueous solutions are the most effective rinsing agents for cleaning the wafer surfaces being processed.

In developing the present invention, consideration was given to the corrosion mechanisms typically encountered in semiconductor wafer processing. For example, the corrosion of aluminum was studied with reference to the following oxidation/-reduction reactions:



Equations 1 and 2 describe the reactions driving the formation of corrosion and corrosion by-products reflected in Equations 3 and 4. As will be seen herein, the approach of the present invention is to remove the oxygen reactant. Further, it is observed that the corrosion rates are affected by the pH of the aqueous solution. One objective of the present invention is to combine both pH control and oxygen removal to form a combined one-step treatment of the aqueous solution brought in contact with the wafers being processed.

Referring now to Figs. 1 and 2, a wafer treatment apparatus according to principles of the present invention is generally indicated at 10. Apparatus 10 includes a process chamber 12 surrounded by related equipment, to form a practical wafer-treating operation. As can be seen in Fig. 2, a robot load/unload area 14 is located adjacent or above the process chamber and includes conventional robotic

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placement equipment (not shown) for inserting and removing semiconductor wafers from process chamber 12. Reference numeral 16 is directed to a portion of wafer treatment apparatus 10 which includes an uninterrupt-  
5 able power supply (UPS) and control means, including a computer, and electronics input/output capability which is accessed by switches and other controls 16 located on the outside of the enclosure cabinet, as can be seen, for example, in Fig.1.

10 Turning now to Fig. 3, the process chamber 12 is shown in greater detail. Although different processes can be carried out with chamber 12, it has found immediate application for immersion cleaning (including rinsing and drying) of semiconductor wafers,  
15 such as wafer 22 shown in Fig. 3. Chamber 12 includes a body generally indicated at 24 comprising a receptacle 26 and an outer, surrounding enclosure 28. Body 24 defines a hollow interior 30 which preferably is hermetically sealed and exhausted to a suitable  
20 control system.

Receptacle 26 is preferably made of quartz material or other non-reactive material and is formed to define a wafer-receiving cavity 34 having an upper opening 36 through which wafers or other workpieces  
25 pass as they are inserted and removed from cavity 34. A weir opening 38 is formed adjacent the upper end of receptacle 26 and directs overflow in a manner to be described below with reference to the schematic diagram of Fig. 4. One or more wafers 22 are supported at  
30 their bottom edge on furniture or support members 42 located adjacent a passageway 44 communicating with a plenum 46 which is located beneath body 24. A fast drain valve 48 is located at the lower end of plenum 46.

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As can be seen in Fig. 3, passageway 44 connects cavity 34 with an interior volume 52 of plenum 46. A fast flow valve 60 and a slow flow valve 62 communicate with interior 52 and are operated to fill  
5 plenum 46 with an aqueous medium, preferably deionized water treated in a manner to be described herein. Also coupled to the interior 52 of plenum 46 is a fast flow valve 66 and a slow flow valve 68, used to fill plenum  
10 46 with a chemical, such as solvents or a non-aqueous rinse solution, such as isopropyl alcohol (IPA). In operation, plenum 46 is first filled with a desired solution, with the level eventually rising past  
passageway 44 to enter cavity 34. The liquid level may be maintained within quartz receptacle 26 at any step  
15 of a process or may intentionally cause overflow to pass through overflow weir 38. Preferably, workpieces and solutions within receptacle 26 are excited by conventional means, such as sonic, preferably ultra-sonic or megasonic transducers 102, to enhance the  
20 cleaning or other processing operations.

An upper wall 72 of body 24 includes a recess for a conventional sealing gasket 74. A plurality of lids, preferably two lids and most preferably three  
25 lids, are hingedly joined to body 24 adjacent upper surface 72 and are selectively movable, one at a time, to sealingly enclose the upper end 36 of receptacle 26. As will be seen herein, each lid is operable to enclose cavity 34 to provide a wide range of environments  
within the receptacle cavity. For example, processing  
30 lid 80 hingedly connected at 82 to body 24 is closed during cleaning or other processing of wafer 22. In order to prevent condensation on the lid inner surface 84, lid 80 is provided with a blanket heater 86. It is generally preferred that the lid 80 confine a  
35 pressurized gas blanket on top of the liquid surface

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within cavity 34. The gas blanket is introduced into the cavity by conventional nozzle means in the process lid or cavity wall. The gas blanket can be comprised of a suitable non-reactive purge gas, such as nitrogen, or, if desired, can be comprised of carbon dioxide so as to provide additional pH control if the liquid surface within cavity 34 is broken, as during a rapid cavity-filling operation. Optionally, the processing lid 80 can include apparatus for purging ambient environment from cavity 34 preparatory to a processing operation.

Drying lid 90 is lowered to engage gasket 74 and enclose upper opening 36 of cavity 34 during wafer drying operations. Lid 90 preferably includes conventional wafer drying equipment of the "MARANGONI" or surface tension gradient drying type, but other types of drying apparatus, such as heat lamps, super heated vapor, or spin drying can also be used. One example of drying lid 90 is given in United States Patent No. 5,634,978, the disclosure of which is incorporated by reference as if fully set forth herein.

The preferred lid 90 includes an assembly 92 of nozzles injecting a final rinse solution, preferably one having a relatively low vapor pressure, such as isopropyl alcohol, and a heated inert drying medium, such as nitrogen gas. A third, load lid 94 is used during load/unload operations and includes an inner surface on which wafer cassettes, carriers or other load/unload equipment may be temporarily placed. However, if working surfaces are otherwise provided, or if sufficiently capable robotic equipment is used for loading and unloading, lid 94 may be rendered unnecessary and can be omitted, if desired.

Referring again to Fig. 2, various components associated with the drying equipment located in

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assembly 92 are identified in Fig. 2 by reference numeral 106. The components 106 are coupled by means not shown, to assembly 92 in lid 90. As mentioned, valves 60, 62 introduce aqueous media into receptacle  
5 26. In order to provide improved control over oxidation reactions with layered, copper-bearing structures carried on wafer 22, the aqueous media in contact with wafer 22 is, according to one aspect of the present invention, treated by an oxygen filter in  
10 the form of an osmotic membrane degasifier indicated by reference numeral 108 in Fig. 2. The aqueous media (preferably conventional deionized water) is passed over a semi-permeable membrane, such as membranes available from Hoechst Celanese for use with their  
15 LIQUI-CEL Membrane Degasifier, the osmotic membrane degasifier preferred in carrying out the present invention. Similar osmotic membrane degasifiers may also be commercially obtained from Pail Corporation of East Hills, New York, under the trade designation  
20 "SEFAREL" and W.L. Gore & Assoc. in Elkton, Maryland under the trade designation "DISSOLVE".

The aqueous media is passed over one side of the semi-permeable membrane in degasifier 108 while a carrier fluid, preferably a gas at a pre-selected  
25 temperature and pressure, is caused to flow over the opposite side of the semi-permeable membrane. The preferred carrier gas, according to the principles of the present invention, may be comprised of one or more components and preferably carries out several purposes.  
30 First, the carrier gas "carries" or "pulls" dissolved oxygen from the aqueous media being treated. Thus, oxygen (or other dissolved gas) from the aqueous media is made to selectively diffuse across the semi-permeable membrane so as to enter the carrier gas  
35 stream located on the opposite side of the membrane.

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Preferably, the flow of carrier gas is set so as to maintain the highest practical diffusion rate across the membrane, preventing oxygen levels on the carrier gas side of the membrane from reaching equilibrium with  
5 the carrier gas.

Optionally, the carrier gas is selected for its ability to diffuse in a reverse direction across the semi-permeable membrane, so as to quiescently inject beneficial additives into solution in the  
10 aqueous media. Most preferably, the carrier gas is selected such that, upon dissolving in the aqueous media it will act to alter the aqueous media pH value in a manner which further precludes corrosion of the wafer structures. The preferred carrier gas of the  
15 present invention comprises a mixture of two gases, one for causing dissolved oxygen in the aqueous media to flow across the osmotic membrane and the second to alter the pH value when introduced into the aqueous media. The first component can be comprised of  
20 virtually any gas or liquid other than oxygen so as to create the desired osmotic pressure across the membrane, and the second component most preferably comprises carbon dioxide, but may also comprise ammonia, nitrous oxide, nitric oxide and carbon  
25 monoxide. Thus, preferably, the carrier gas of the present invention employed for use with semiconductor materials comprises a mixture of carbon dioxide and nitrogen gas. This carbon dioxide mixture is one example of a carrier gas meeting one requirement of the  
30 present invention, that of "pulling" oxygen from the aqueous media through the semi-permeable membrane, while passing an effective pH modifier through the membrane in an opposite direction.

The carrier gas can provide further  
35 functions. For example, it has been observed that gas

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entrained in the aqueous media provides a more efficient coupling of agitation energy, such as sonic energy, including energy at ultrasonic and megasonic (i.e., megahertz) frequency regimes. As pointed out  
5 above, dissolved oxygen can be a poor choice for agitation enhancement. However, with the present invention, a benign gas can be dissolved in the aqueous media, upon its passage through the osmotic membrane.

Once in solution with the aqueous media, the  
10 carbon dioxide emerging through the membrane removes  $\text{OH}^-$  shown in the above equations, and especially Equation 3. However, unlike carbon dioxide sparging or bubbling, potentially contaminating particles are not introduced into the wafer-contacting aqueous media.  
15 Further advantages over sparging techniques are also made possible by the present invention. For example, by passing through the semi-permeable membrane of the present invention, carbon dioxide is introduced into the aqueous media in a finer, i.e., physically smaller,  
20 form. Accordingly, carbon dioxide is more completely dissolved in the aqueous media and is more quickly and thoroughly mixed. Further, with the present invention, carbon dioxide is introduced into the aqueous media quiescently, without bubbles. In addition to slowing  
25 or otherwise impairing dissolving of the encapsulated  $\text{CO}_2$  gas, bubbles introduced by sparging or the like bubbling technique might be carried to the wafer surface to form an effective barrier, at least partly blocking intimate contact of the wafer surface with the  
30 treating solution.

In order to provide a wide range of control of pH values, the preferred carrier gas, as mentioned, comprises a mixture of carbon dioxide and a diluent, such as nitrogen gas, which allows the oxygen transfer  
35 rate to continue across the membrane while holding the

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aqueous media pH value at a constant level. As can be seen from the above, the CO<sub>2</sub> gas is introduced into the aqueous media to provide pH control. The present invention also contemplates the introduction of  
5 chemicals passing through the osmotic membrane to achieve desired objectives other than pH control. For example, a desired surfactant may be introduced in liquid or gaseous form in the carrier stream and, upon passing through the osmotic membrane, will be  
10 quiescently added to the aqueous media. If desired, additional control may be provided by employing other, conventional pH control methods directly in the process chamber. For example, a carrier gas mixture of 4% hydrogen gas and 96% nitrogen gas can be used to  
15 provide a more reducing environment, which is less likely to permit corrosion. As a further example, an injection apparatus can be provided within cavity 34 to introduce a buffer or ion exchange solution. Optionally, an acid or base drip can be added to one of  
20 the lids covering the cavity.

In addition to the above equations, consideration is also given to the increasing use of copper and copper alloys as structures layered on semiconductor substrates. From a device manufacturer's  
25 standpoint, increased copper content provides increased conductivity and hence increased speed of electronic operation. The demand for copper content of copper/aluminum alloys is steadily increasing and it is possible that metal lines formed on semiconductor  
30 substrates may be comprised entirely of copper metal. As is well known, even small percentages of copper undergo substantial corrosion when contacted with water containing dissolved oxygen. When such small amounts of copper (components greater than 1% of the total  
35 alloy) are added to aluminum, an observed galvanic



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reaction between copper and aluminum operates to seriously increase the corrosion rate of the aluminum component.



5                   Once the aluminum component becomes positively charged, the electrons are attracted in the p-orbital of the rinse water  $\text{O}_2$  molecule. By effectively removing dissolved oxygen from the aqueous media, the present invention eliminates these types of  
10 corrosion reactions.

                  It has also been observed in carrying out the present invention, that the corrosion reaction rate displays photochemical sensitivity. Attempts to quantify the photoreactivity of the various corrosion  
15 reactions have not been studied in detail, but even so, the observed photoreactivity role is pronounced in conventional semiconductor cleaning operations. The process chamber 12 is constructed such that the interior of receptacle 26 is sealed in a light-tight  
20 as well as an air-tight condition, using lids which carry out multiple functions beyond merely blocking ambient light.

                  As mentioned above, wafers 22 to be processed may be sprayed, but are preferably immersed in solution  
25 contained within receptacle 26. This provides several advantages. Due to the chemical sensitivity of materials employed, and ever tightening constraints on process parameters, management of so-called "backside" wafer contamination is becoming increasingly important  
30 if wafer losses are to be controlled. By providing an immersion cleaning of wafers 22, issues of backside contamination are eliminated in a cost effective rapid

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manner, since all exposed surfaces of the wafer are cleaned simultaneously.

Further, with the present invention, dislodged particles are managed with greater control so as to prevent their re-introduction on the wafer surface. For example, referring to Figs. 2 and 4, tanks 110, 112 are located adjacent process chamber 12 and are coupled to the process chamber with a plurality of supply and return lines. Tank 110 is coupled to plenum 46 by a return line 116 and by a supply line 118 which includes a pump 120 and filter 122. A second return line 124 couples tank 110 to weir outlet 38. Tank 112 is connected to plenum 46 through return line 126 and through supply line 128 associated with pump 130 and filter 132. A second return line 134 couples tank 112 to weir outlet 38. Tanks 110, 112 have supply inlets 140, 142 to a bulk chemical source (not shown).

Referring to the bottom right corner of Fig. 4, a deionized water inlet 150 and a carbon dioxide mixture inlet 152 are provided for the osmotic membrane degasifier 108. The carbon dioxide mixture or other carrier gas entering inlet 152 passes across the membrane internal to degasifier 108 and exits through exhaust 154. A portion of the carrier gas, along with the water introduced by inlet 150, exits through line 156 which is coupled to valves 60, 62. Preferably, inlets 150, 152 include temperature control (e.g., heating) capability coupled to controller 304. In addition to providing control of the aqueous media in cavity 34, heating control at inlets 150, 152 controls the diffusion rates and bi-directional selectivity of the osmotic membrane.

Referring to the upper right-hand portion of Fig. 4, drying equipment 106 includes a rinse agent tank 160 and a pump 162 which are coupled to assembly

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92 mounted in lid 90. As mentioned, the rinse agent preferably comprises isopropyl alcohol. The drying gas, preferably N<sub>2</sub>, enters through inlet 164 and is heated in heater 166, thereafter being conducted  
5 through line 168 to assembly 92 in lid 90.

As noted above, it is preferred that all wafer-contacting chemistries are introduced into cavity 34 from plenum 46. In this arrangement, points of entrapment are eliminated as are direct chemical  
10 connections to receptacle 26, thereby avoiding the attendant possibility of mis-operation. As will be seen below, it is generally preferred that cavity 34 be operated as a recirculating immersion process chamber as well as an overflow immersion rinse bath. Although  
15 not preferred for the treatment of semiconductor wafers, cavity 34 can be operated in a spray contact or waterfall mode, with conventional nozzles located in the interior of cavity 34 and/or the lids associated therewith.

As can be seen from the above description of Fig. 4, several recirculation loops are provided with the arrangement of the present invention and it is contemplated that the treatment apparatus may comprise a totally closed system. However, it may also be  
25 advantageous from time to time to discard certain portions of the processing or rinsing agents employed and connections to an industrial waste water drain are provided by line 172 (exiting a manifold at the outlet of plenum 46) and line 174 (coupled to the weir discharge 38). Connections to a separate solvent drain  
30 are provided by line 176 exiting plenum 46 and line 178 coupled to tank weir outlet 38.

As will be appreciated from the foregoing, chamber 12 can be operated in a number of different  
35 ways. For example, wafer treatment can be limited to

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post solvent wafer rinse. However, it has been found unnecessary to perform residue-removing solvent cleaning at a separate location. Rather, residue is preferably removed from the wafer using solvent in chamber 12, followed by a solvent-removing rinse and concluding with a wafer drying operation. Initially, cavity 34, passageway 44 and plenum 46 are emptied, cleared of all liquids. If desired, a purge gas can be employed, filling the cavity, passageway and plenum.

10 In preparation for a wafer transport operation, load lid 94 is opened and one or more wafers 22 are inserted in cavity 34, so as to rest on furniture supports 42. In an optional pre-treating step, the empty plenum 46 is then filled with a first

15 solvent solution, preferably taken from tank 110 and passed through filter 122. Solvent is introduced so as to eventually fill plenum 46, passageway 44 and the interior or cavity of receptacle 26. Tank 110 preferably contains used solvent, captured from a

20 previous secondary solvent cleaning operation, as will be seen herein. This initial contact with the wafer causes the highest concentration of residue and contaminating particles to enter into solution within cavity 34. It is anticipated that, in many commercial

25 operations, this initial pre-treatment solution will be discarded. Depending upon the flow conditions within cavity 34, the initial pre-treating solution may also exit cavity 34 through overflow weir 38. Alternatively, cavity 34, passageway 44 and plenum 46 may be

30 drained by line 176.

In certain instances, the pre-treatment operation may be unnecessary, in which case pump 120 is energized so as to withdraw used solvent from tank 110, which, after exiting filter 122, fills plenum 46 and

35 ultimately cavity 34. After a sufficient period of

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ultrasonic agitation, the solvent is either returned to tank 110 through line 116 or is discharged to the solvent drain through line 176. It is generally preferred during all stages of wafer cleaning that  
5 wafer 22 be maintained fully immersed and further that cavity 34 be filled so as to cause a controlled overflow through weir 38. Overflow solvent can be returned to tank 110 through line 124 or the overflow can be discharged to solvent drain through line 178.

10 If desired, conventional particle counters 300 (see Fig. 4) such as those commercially available from Particle Measuring Systems (PMS) located at Boulder, Colorado can be employed to monitor contents of cavity 34 to aid in the decision whether to retain  
15 or discard the overflow and/or the cavity contents. Alternatively, conventional chemical monitoring systems 302 may be coupled to controller 304, to sample the weir overflow to detect the presence or concentration of a residue component in order to provide information  
20 to controller 304 indicating the real time concentration of residue in solution. Such indications can be used to detect when rinsing of solvent is complete. According to the concentrations of residue indicated, the overflow residue can, under operation in controller  
25 304, be either retained in tank 110 or discarded. Output indications can also control any amount of contamination - diluting fresh chemistry that may be added to tank 110 through line 140.

At the conclusion of the first cleaning  
30 stage, with the reused solvent being withdrawn from the plenum 46 and tank cavity 34, "cleaner" solvent in tank 112 is passed through pump 130 and filter 132 to plenum 46 and the level is allowed to rise, filling cavity 34, fully immersing wafer 22 and causing a controlled  
35 overflow through weir outlet 38. Weir overflow may

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be returned through line 134 to tank 112 or may be discharged to a solvent drain through line 178. At the conclusion of the second stage of wafer cleaning, the wafer may be immersed, sprayed, washed or otherwise  
5 "reused" with virgin solvent from a bulk supply. The tank cavity passageway 44 and plenum 46 are then drained of all solvent. The solvent is preferably returned to tanks 110 and/or 112 through lines 116, 126 but may be discharged to a solvent drain through line  
10 176, if desired.

Thereafter, wafer 22 is rinsed with an aqueous rinse solution to remove solvent from the wafer surface, wafer cavities and other structures carried on the wafer substrate. An aqueous media such a deionized  
15 water is processed in osmotic membrane degasifier 108, as described above. A flow of deionized water enters through inlet 150 and a flow of carbon dioxide carrier gas enters the degasifier through inlet 152. Oxygen enriched carrier gas exits degasifier 108 through line  
20 154 and the oxygen-depleted, pH-balanced deionized water exits degasifier 108 on line 156. The aqueous solution, thus treated, may be stored on site, if desired. Preferably, however, the aqueous solution is used on demand, as needed. As with other solutions  
25 contacting the device being treated, the modified deionized water fills plenum 46, passageway 44 and cavity 34, immersing wafer 22. Preferably, a controlled overflow is maintained through weir opening 38, being directed through a manifold coupled to exit line  
30 174, thereby being passed to an industrial waste water drain. If desired, overflow can be filtered and redirected through pumping (not shown) to a deionized water reclaim inlet 186, although this has been found to be unnecessary due to the cost efficiencies of  
35 employing deionized water as a rinse agent.

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Turning now to Figs. 5-8, the preferred solvent exposure will be briefly considered. Fig. 5 shows an initial wafer contacting operation in which reused solvent from tank 110 fills cavity 34. . This  
5 initial contact with the wafer contains the majority of dissolved polymer, with polymer concentrations substantially higher than those found in tank 110. Accordingly, it may be desired to discharge the initial contacting solvent to the solvent drain as indicated.  
10 Thereafter, the overflow solvent is recirculated back to tank 110 and preserved for reasons of economy. If desired, the solvent could also be directed to a suitable solvent drain.

Although the solvent represented in Fig. 6 is  
15 reused and therefore contains certain concentrations of dissolved residues, the concentrations of residue are relatively small compared to the concentrations obtained upon initial wafer contact as considered above with reference to Fig. 5. It is generally preferred  
20 that most, if not all, of the residues on the wafer be removed in the step indicated in Fig. 6, i.e., with reused solvent.

Only after the residues are removed from the surface of the wafer being treated is cleaner solvent  
25 applied to the wafer, as indicated in Fig. 7. Use of fresh solvent eliminates the possibility of dropping dissolved polymer residue out of solution or interrupting the suspension of polymer in solvent which is not yet filtered. The preferred purpose of introducing  
30 cleaner solvent from tank 112 is to remove dirty solvent prior to recirculating the chemistry. As indicated in Fig. 7, it is preferred to capture the "cleaner" solvent from tank 112 in tank 110, for use on the next cleaning cycle.

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As will be appreciated, the chemistry now present in contact with the wafer is cleaner than conventional dual tank bench configurations, because the volume within the tank is continually topped off with fresh chemistry from a bulk source. As can be seen from the diagram of Fig. 4, it is also possible to use virgin solvent chemistry exclusively, prior to the aqueous rinse step.

Referring to Fig. 8, as a final solvent cleaning step, fresh, unused solvent is introduced and recirculated with respect to tank 112. It is preferred that solvent filling the cavity, passageway and plenum are returned to tank 112 for future use. Thereafter, the aqueous rinse and drying steps described above are carried out. During this time, tank 112 is "topped off" from a bulk solvent source, if desired. As will be appreciated, fresh solvent introduced into tank 112 will have benefit of a substantial residence time for any desired mixing, heating, or other temperature control prior to its application in a subsequent process cycle.

In order to maintain the proper chemical component ratios of the solvent as long as possible, the present invention allows the cleaning step to be carried out with a minimum exhaust and purge, which might otherwise cause a loss of quality or quantity of solvent due to evaporation or decomposition associated with oxygen and water content in surrounding air. Thus, as can be seen, the present invention provides improved chemistry management by controlling the chemistry environment during a cleaning operation.

As has been noted above, certain variations and alternative arrangements are possible with the methods and apparatus according to the principles of the present invention. If desired, other alternative



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arrangements can also be readily employed with the present invention, using conventional equipment and techniques. For example, operation of the osmotic membrane degasifier 108 can be automated using  
5 conventional techniques so as to minimize consumption of carrier gas. For example, as mentioned, it is preferred that a mixture of carbon dioxide and nitrogen gas be used for the carrier, at a flow rate which assures adequate diffusion rates of oxygen across the  
10 membrane.

If desired, conventional metering 308 to sense dissolved oxygen can be provided on line 156 and the flow rates of the carrier gas at inlet 152 can be adjusted with control signals applied to N<sub>2</sub> and CO<sub>2</sub> flow  
15 controllers 312, 314, respectively. For example, if objectionable oxygen levels are detected in line 156, the flow rate of carrier gas can be increased in order to increase osmotic pressure, thereby withdrawing higher rates of dissolved oxygen from incoming aqueous  
20 solution. On the other hand, if dissolved oxygen content in line 156 is sufficiently low, it may be possible to reduce the input flow of one or more carrier gas components and still achieve the desired levels of oxygen removal in line 156.

25 Further, related variations are also possible. For example, the carbon dioxide and nitrogen components of the carrier gas can be mixed as needed and fed into inlet 152. Conventional pH meters can be incorporated in metering 308 to sense the pH of aqueous  
30 media in line 156 and the CO<sub>2</sub> component of the carrier gas can be adjusted by operation of flow controller 314 to attain the desired pH level. Any undesired reaction in osmotic pressure (needed to remove dissolved oxygen) can be effectively dealt with by independently ad-  
35 justing the nitrogen gas flow component (by signals to

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flow controller 312), since both carbon dioxide and nitrogen gas components of the carrier gas are effective in maintaining the desired osmotic pressure needed for effective oxygen removal from the aqueous solution in degasifier 108. If desired, the pH monitoring output and dissolved oxygen monitoring outputs from metering 308 can be considered together either by an operator or more preferably by computer controlled automation 304 to vary the flow rates of the components of carrier gas entering inlet 152. Of course, such automated control could operate to prevent aqueous media in line 156 from entering process chamber 12 if the dissolved oxygen and/or pH levels exceed predefined control points.

As mentioned above, particle counters 300 and chemical monitoring sensors 322 of predictors indicating the concentration of dissolved residue can be employed in cavity 34 or in the effluent of overflow exiting weir 38. As indicated in the above discussion, it is contemplated that automated control attention be given to the varying concentrations of contaminant particles and residue levels in cavity 34, and that control steps be taken to segregate (preferably discard) materials containing unacceptably high concentrations of contaminant particles and/or dissolved residue.

Contaminant levels (either particles or dissolved residue) can be estimated based on their residence time in contact with the wafer or other workpieces immersed within cavity 34. For example, consideration is given to the fact that the material filling cavity 34 be inputted in the plenum 46 at a rate so as to assure a desired rate of overflow passing through overflow weir 38. Overflow materials initially appearing at weir 38 can, for an initial period of

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time, be diverted away from a recirculation loop or storage container and thus be prevented from coming into contact with lesser-contaminated solution.

However, using conventional automation  
5 techniques, greater efficiencies can be obtained by directly monitoring the contamination levels within cavity 34 and/or effluent from overflow weir 38. Particle counters and/or automated chemical monitors of dissolved residue can be employed to provide a more  
10 efficient use of solution by preventing the unnecessary disposal of solution initially contacting the wafer surface. In this manner, greater flexibility of operation is possible and wafers of differing compositions and surface properties can be accommodated  
15 with a single routine production schedule.

Further, with the introduction of automated metering and other controls, it may be possible to consider a refurbishing of treatment materials employed in the process chamber. For example, decisions can be  
20 made based upon the contaminant levels (either particles in solution or dissolved chemistries) as to whether it is cost effective to attempt to reclaim the solution in question. For example, it may be observed that solvents and rinse solutions contain acceptable  
25 levels of chemical components, but unfortunately carry unacceptably high levels of contaminant particles. The solutions in question can be directed through conventional filtering equipment and retested to certify their acceptability for re-introduction in  
30 subsequent processing stages. It may also be possible to perform the same reclamation, by chemically treating the solution in question so as to remove or reduce unwanted dissolved chemistries.

Automated instrumentation can also take into  
35 account the need for make-up of solutions flowing

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through tanks 110 or 112, for example. Calculations can be made as to the net effect on ultimate contaminate levels and it may be possible from time to time to prevent the unnecessary discarding of process solutions by diluting with fresh chemistries, thereby providing savings relating not only to the cost of replacement solutions but also of waste handling. It will be appreciated by those skilled in the art that such automated instrumentation can be provided using conventional techniques, in a space-efficient manner which would not contribute considerably to the space requirements for the processing equipment.

It will be readily appreciated by those skilled in the art that the oxygen filter (e.g., osmotic membrane degasifier), along with optional automated controls, can be used in stand-alone mode to provide a stored quantity of treated aqueous material. Further, the oxygen filter can be incorporated in arrangements other than those shown herein. For example, conventional wafer polishing operations can benefit from the incorporation of the oxygen filter according to principles of the present invention, and it will be appreciated in this regard that substantial reduction of wafer handling is thereby made possible. If desired, further advantages may be obtained by combining the oxygen filter and process chamber of the present invention, incorporating the combination, for example, in existing wafer processing operations.

If desired, variations in the process chamber are also contemplated by the present invention. As mentioned above, wafer processing benefits from a light-tight closed environment and a flexibility of operation and reduction in wafer handling has been achieved by incorporating a plurality of different lid arrangements with a common receptacle. It is possible,

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however, to adapt the receptacle for continuous, rather than batch operations. For example, a conveyor belt can be made to pass through the process receptacle and can include depressed portions for immersing articles  
5 carried on the conveyor belt beneath fluid levels maintained within the receptacle. Such arrangements may be particularly attractive for photographic operations, for example.

The drawings and the foregoing descriptions  
10 are not intended to represent the only forms of the invention in regard to the details of its construction and manner of operation. Changes in form and in the proportion of parts, as well as the substitution of  
15 equivalents, are contemplated as circumstances may suggest or render expedient; and although specific terms have been employed, they are intended in a generic and descriptive sense only and not for the purposes of limitation, the scope of the invention being delineated by the following claims.

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WHAT IS CLAIMED IS:

1. Apparatus for processing a workpiece, comprising:

5 a treatment chamber defining a cavity for receiving the workpiece and a device opening through which said workpiece is passed into and out of the cavity;

an osmotic membrane degasifier defining a degasifier cavity, a membrane dividing the degasifier  
10 cavity into first and second parts, a aqueous solution inlet and a aqueous solution outlet associated with said first part to direct aqueous solution into contact with one side of the membrane, and a carrier fluid inlet and a carrier fluid outlet associated with said  
15 second part to direct carrier fluid into contact with the other side of the membrane;

and the aqueous solution outlet coupled to the treatment chamber.

2. The apparatus of claim 1 further  
20 comprising a plenum coupled to the treatment chamber and defining a mixing chamber coupled to the aqueous solution outlet.

3. The apparatus of claim 1 further comprising a chemical opening for introducing a  
25 processing chemical into the mixing chamber.

4. . The apparatus of claim 1 further comprising a plurality of covers hingedly connected to said treatment chamber to selectively cover said device opening.

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5. The apparatus according to claim 4 further comprising fluid blanket means for inserting a gas blanket enclosed within said cavity.

6. The apparatus according to claim 5 wherein said gas blanket means is disposed in one of said covers.

7. The apparatus according to claim 5 wherein said gas blanket is at least partially comprised of carbon dioxide gas.

8. The apparatus of claim 4 wherein at least one of said covers is light blocking.

9. The apparatus of claim 4 wherein one of said covers includes a heater means to prevent condensation.

10. The apparatus of claim 4 wherein one of said covers includes means for injecting a rinse agent into said chamber.

11. The apparatus of claim 10 wherein said one cover further includes means for directing a drying gas into said chamber.

12. The apparatus of claim 1 wherein said treatment chamber includes a cavity wall defining said cavity, said apparatus further comprising agitation means coupled to at least one of said cavity wall and said aqueous solution.

13. The apparatus according to claim 12 wherein said agitation means comprises ultrasonic

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transducer means coupled to at least one of said cavity wall and said aqueous solution.

14. The apparatus according to claim 12 wherein said agitation means comprises megahertz  
5 frequency transducer means coupled to at least one of said cavity wall and said aqueous solution to impart agitation energy thereto.

15. The apparatus of claim 1 wherein:  
said treatment chamber further defines an  
10 overflow weir.

16. The apparatus of claim 15 further comprising:  
a storage tank; and  
means for coupling said weir to said storage  
15 tank.

17. The apparatus of claim 16 further comprising:  
one of said treatment chamber and said plenum defining a return outlet; and  
20 means for coupling said return outlet to said storage tank.

18. The apparatus of claim 17 further comprising a plenum coupled to the treatment chamber, said plenum defining a mixing chamber coupled to the  
25 aqueous solution outlet and containing said return outlet.

19. The apparatus of claim 1 further comprising:



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oxygen sensor means for sensing the oxygen content in the aqueous solution outlet; and

flow control means coupled to said sensor and responsive thereto for controlling the flow of carrier  
5 fluid at said carrier fluid inlet.

20. The apparatus of claim 19 wherein said carrier fluid comprises a composition of first-and second gases and said flow control means comprises means for controlling the flow of each of said  
10 components.

21. The apparatus according to claim 1 further comprising particle counting means disposed in said treatment chamber for counting the particles transferred from said workpiece to said aqueous fluid  
15 in said cavity.

22. A method for treating a workpiece with an aqueous solution, comprising:

providing a carrier fluid comprising at least one component;

20 passing said aqueous solution and said carrier fluid through an osmotic membrane degasifier having a membrane, so as to draw oxygen from said aqueous solution through said membrane to said carrier fluid;

25 providing a treatment chamber;  
at least partly filling said treatment chamber with said aqueous solution from said osmotic membrane degasifier; and

30 at least partly immersing said workpiece in said aqueous solution.

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23. The method of claim 22 wherein said step of passing said carrier fluid through said osmotic membrane degasifier also passes carrier fluid through said membrane, introducing at least one component of  
5 said carrier fluid into said aqueous solution so as to control the pH of said aqueous solution

24. The method of claim 23 wherein said carrier fluid includes carbon dioxide.

25. The method of claim 22 further  
10 comprising the steps of:  
    providing a treatment chamber defining a cavity for receiving the workpiece;  
    inserting the workpiece into the cavity; and  
    filling the cavity with said aqueous solution  
15 so as to immerse said workpiece in said aqueous solution.

26. The method of claim 25 further comprising the steps of:  
    providing a plenum defining a mixing chamber  
20 coupled to said treatment chamber; and  
    the step of filling the cavity with said aqueous solution comprises the step of passing aqueous solution through said mixing chamber prior to entering said cavity.

25           27. The method according to claim 25 further comprising the step of sealing said cavity with a light-tight cover.

28. The method according to claim 25 further comprising the step of enclosing the cavity with a  
30 heated cover.

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29. The method according to claim 25 further comprising the step of enclosing the cavity with a cover and introducing a gas blanket in said cavity.

30. The method according to claim 29 wherein  
5 said gas blanket is at least partly comprised of carbon dioxide.

31. The method according to claim 25 further comprising the step of providing a cover to enclose said cavity and injecting a rinse agent from said  
10 cavity into said treatment chamber.

32. The method according to claim 25 further comprising the steps of providing a cover to enclose said cavity, emptying said cavity, and directing a drying gas from said cover into said treatment chamber.

33. The method of claim 22 further  
15 comprising the step of agitating the aqueous solution to enhance the treatment of workpieces therein.

34. The method according to claim 33 wherein  
20 said agitating step comprises exciting said aqueous solution with an ultrasonic frequency.

35. The method according to claim 33 wherein said agitating step comprises exciting said aqueous solution with sonic energy in the megahertz frequency range.

36. The method according to claim 22 further  
25 comprising the step of providing an overflow weir in said treatment chamber and filling said treatment

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chamber with said aqueous solution so as to overflow a portion of said aqueous solution through said weir.

37. The method according to claim 36 further comprising the steps of providing a storage tank and  
5 coupling the flow from said weir to said storage tank.

38. The method according to claim 22 further comprising the step of monitoring the oxygen content of said aqueous solution from said osmotic membrane degasifier.

10 39. The method according to claim 38 further comprising the step of controlling the flow of carrier fluid through said osmotic membrane degasifier in response to the oxygen level sensed in said aqueous solution from said osmotic membrane degasifier.

15 40. The method according to claim 39 wherein the step of providing a carrier fluid comprises the step of providing a plurality of carrier fluid components and mixing said carrier fluid components together to form said carrier fluid.

20 41. The method according to claim 40 wherein the step of controlling the flow of carrier fluid entering said osmotic membrane degasifier comprises the step of individually controlling the carrier fluid components which are mixed together to form said  
25 carrier fluid.

42. The method according to claim 22 wherein said step of contacting the workpiece with said aqueous solution from said osmotic membrane degasifier

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comprises immersing the workpiece in said aqueous solution.

43. The method according to claim 22 wherein said step of contacting the workpiece with said aqueous solution from said osmotic membrane degasifier comprises spraying the workpiece with said aqueous solution.

44. The method according to claim 22 wherein said step of contacting the workpiece with said aqueous solution from said osmotic membrane degasifier comprises passing said aqueous solution over the workpiece.

45. A method for treating opposed major surfaces of a semiconductor device, comprising:  
providing a treatment chamber defining a cavity for receiving the semiconductor device;  
providing a carrier fluid;  
providing an aqueous solution;  
inserting the semiconductor device into the cavity;  
passing said aqueous solution and said carrier fluid through an osmotic membrane degasifier having a membrane so as to draw oxygen from said aqueous solution through said membrane to said carrier fluid and so as to introduce carrier fluid through said membrane, into said aqueous solution so as to control the pH of said aqueous solution; and  
contacting said semiconductor wafer with aqueous solution from said osmotic membrane degasifier.

46. The method of claim 45 further comprising the step of drying the said semiconductor

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device by emptying the cavity of said aqueous fluid and passing heated fluid over the surfaces of said semiconductor device.

47. The method of claim 46 wherein said step  
5 of drying said semiconductor device further comprises the step of spraying a rinse chemical on the major surfaces of said semiconductor device.

48. The method according to claim 45 further comprising the steps of:  
10 providing a process cover with heater means for heating the process cover;  
providing a drying cover with means for directing a stream of drying gas;  
providing said treatment chamber with a  
15 device opening through which said semiconductor device is passed into and out of said cavity;  
covering said device opening with said process cover during treatment of said semiconductor device; and  
20 withdrawing said process cover from said device opening and covering said device opening with said drying cover during drying of said semiconductor device.

49. The method according to claim 45 further  
25 comprising the step of sonically exciting at least one of said treatment chamber and said aqueous solution with sonic energy in one of said ultrasonic and said megahertz frequency ranges.

50. The method according to claim 45  
30 further comprising the steps of providing an overflow weir and filling said cavity with aqueous solution so

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as to immerse said semiconductor device with said aqueous solution and so as to overflow aqueous solution through said weir.

51. The method according to claim 50 further  
5 comprising the steps of providing a storage tank and coupling the overflow through said weir to said storage tank.

52. The method according to claim 48 further  
10 comprising the steps of monitoring the oxygen content of said aqueous solution from said osmotic membrane degasifier.

53. The method according to claim 52 further  
comprising the step of controlling the flow of carrier  
15 fluid through said osmotic membrane degasifier in response to measurements of oxygen in said aqueous solution.

54. The method according to claim 53 wherein  
said carrier fluid is comprised of a plurality of  
carrier fluid components which are mixed together to  
20 comprise said carrier fluid.

55. The method according to claim 54 wherein  
said step of controlling the flow of carrier fluid  
comprises the step of individually controlling the flow  
of carrier fluid components mixed together and inputted  
25 into said osmotic membrane degasifier.

56. The method of claim 45 further  
comprising the step of providing said carrier fluid  
with a carbon dioxide component.

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57. The method according to claim 45 further comprising the steps of counting particles transferred from said semiconductor device to said aqueous solution.

5 58. The method according to claim 56 further comprising the step of withdrawing at least a portion of said aqueous solution from said receptacle in response to said counting of particles transferred from said semiconductor device to said aqueous solution.

10 59. The method of claim 50 further comprising the steps of:  
providing a plenum defining a mixing chamber coupled to said treatment chamber; and  
the step of filling the cavity with said  
15 aqueous solution comprises the step of passing aqueous solution through said mixing chamber prior to entering said cavity.

60. The method according to claim 45 further comprising the step of enclosing the cavity with a  
20 cover and introducing a gas blanket in said cavity.

61. The method according to claim 60 wherein said gas blanket is at least partly comprised of carbon dioxide.

62. Apparatus for processing a semiconductor  
25 device, comprising:

a treatment chamber defining a cavity for receiving the semiconductor device with a device opening through which said semiconductor device is passed into and out of the cavity;



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a plenum coupled to the treatment chamber and defining a mixing chamber including a aqueous solution inlet opening for introducing aqueous solution into the mixing chamber and a nonaqueous solvent opening for  
5 introducing a nonaqueous solvent into the mixing chamber; and

an osmotic membrane degasifier defining a degasifier cavity, a membrane dividing the degasifier cavity into first and second parts, an aqueous solution  
10 inlet and a aqueous solution outlet associated with said first part, and a carrier fluid inlet and a carrier fluid outlet associated with said second part, with the aqueous solution outlet coupled to the aqueous solution inlet opening of said plenum.

15 63. The apparatus of claim 62 further comprising a plurality of covers hingedly connected to said treatment chamber to selectively cover said device opening.

20 64. The apparatus of claim 63 wherein at least one of said covers is light blocking.

65. The apparatus of claim 63 wherein one of said covers includes a heater means to prevent condensation.

25 66. The apparatus of claim 63 wherein one of said covers includes means for injecting a rinse agent into said chamber.

67. The apparatus of claim 66 wherein said one cover further includes means for directing a drying gas into said chamber.

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68. The apparatus of claim 62 wherein said treatment chamber includes a cavity wall defining said cavity, said apparatus further comprising sonic agitation means coupled to one of said cavity wall and  
5 said aqueous solution.

69. The apparatus of claim 62 wherein said treatment chamber further defines an overflow weir.

70. The apparatus of claim 69 further comprising:  
10 a storage tank; and  
means for coupling said weir to said storage tank.

71. The apparatus of claim 70 further comprising:  
15 one of said treatment chamber and said plenum defining a return outlet; and  
means for coupling said return outlet to said storage tank.

72. The apparatus of claim 71 further  
20 comprising a plenum coupled to the treatment chamber, said plenum defining a mixing chamber coupled to the aqueous solution outlet and containing said return outlet.

73. The apparatus of claim 62 further  
25 comprising:  
oxygen sensor means for sensing the oxygen content in the aqueous solution outlet; and  
flow control means coupled to said sensor and responsive thereto for controlling the flow of carrier  
30 fluid at said carrier fluid inlet.

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74. The apparatus of claim 73 wherein said carrier fluid comprises a composition of first-and second fluids and said flow control means comprises means for controlling the flow of each of said fluid components.

75. The apparatus according to claim 62 further comprising particle counting means disposed in said treatment chamber for counting the particles transferred from said workpiece to said aqueous fluid in said cavity.

76. A method for cleaning opposed major surfaces of a semiconductor device, comprising:  
providing a cleaning chamber defining a cavity or receiving the semiconductor device;  
inserting the semiconductor device into the cavity;  
filling the cavity with a first solvent so as to immerse said semiconductor device in said first solvent while exciting said chamber with ultrasonic energy so as to transmit said ultrasonic energy through said first solvent to said semiconductor device;  
emptying said cavity of said first solvent;  
filling the cavity with a second solvent so as to immerse said semiconductor device in said second solvent while exciting said chamber with ultrasonic energy so as to transmit said ultrasonic energy through said second solvent to said semiconductor device;  
emptying said cavity of said second solvent;  
providing an aqueous solution;  
providing a carrier fluid containing carbon dioxide  
passing said aqueous solution and said carrier fluid through an osmotic membrane degasifier

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having a membrane, so as to draw oxygen from said aqueous solution through said membrane to said carrier fluid and so as to introduce carbon dioxide gas through said membrane, into said aqueous solution so as to  
5 control the pH of said aqueous solution.

filling the cavity with a aqueous solution from said osmotic membrane degasifier so as to immerse said semiconductor device in said aqueous solution while exciting said chamber with ultrasonic energy so  
10 as to transmit said ultrasonic energy through said aqueous solution to said semiconductor device;

emptying said cavity of said aqueous solution:

drying the major surfaces of conductor  
15 device; and

removing said semiconductor device from said cavity.

77. The method of claim 76 wherein said step of drying the said semiconductor device comprises the  
20 step of passing heated fluid over the surfaces of said semiconductor device.

78. The method of claim 76 wherein said step of drying said semiconductor device further comprises the step of spraying a rinse agent on the major  
25 surfaces of said semiconductor device.

79. The method according to claim 76 further comprising the steps of:

providing a process cover with heater means for heating the process cover;

30 providing a drying cover with means for directing a stream of drying gas;

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providing said cleaning chamber with a device opening through which said semiconductor device is passed into and out of said cavity;

covering said device opening with said  
5 process cover during rinsing of said semiconductor device; and

withdrawing said process cover from said device opening and covering said device opening with said drying cover during cleaning of said semiconductor  
10 device.

80. The method of claim 76 further comprising the steps of:

providing a plenum defining a mixing chamber coupled to said treatment chamber; and  
15 the step of filling the cavity with said aqueous solution comprises the step of passing aqueous solution through said mixing chamber prior to entering said cavity.

81. The method according to claim 76 further  
20 comprising the step of sealing said cavity with a light-tight seal.

82. The method according to claim 76 further comprising the step of enclosing the cavity with a heated lid.

83. The method according to claim 80 further  
25 comprising the step of withdrawing at least a portion of said first solvent from said cavity and passing said withdrawn portion of said first solvent through said mixing chamber for reintroduction into said cavity.

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84. The method according to claim 80 further comprising the step of withdrawing at least a portion of said second solvent from said cavity and passing said withdrawn portion of said second solvent through  
5 said mixing chamber for reintroduction into said cavity.

85. The method according to claim 80 further comprising the step of withdrawing at least a portion of said aqueous solution from said cavity and passing  
10 said withdrawn portion of said aqueous solution through said mixing chamber for reintroduction into said cavity.

86. The method according to claim 76 further comprising the step of providing an overflow weir in  
15 said treatment chamber and filling said treatment chamber with said aqueous solution so as to overflow a portion of said aqueous solution through said weir.

87. The method according to claim 86 further comprising the steps of providing a storage tank and  
20 coupling the flow from said weir to said storage tank.

88. The method according to claim 76 further comprising the step of monitoring the oxygen content of said aqueous solution from said osmotic membrane degasifier.

25 89. The method according to claim 88 further comprising the step of controlling the flow of carrier fluid through said osmotic membrane degasifier in response to the oxygen level sensed in said aqueous solution from said osmotic membrane degasifier.

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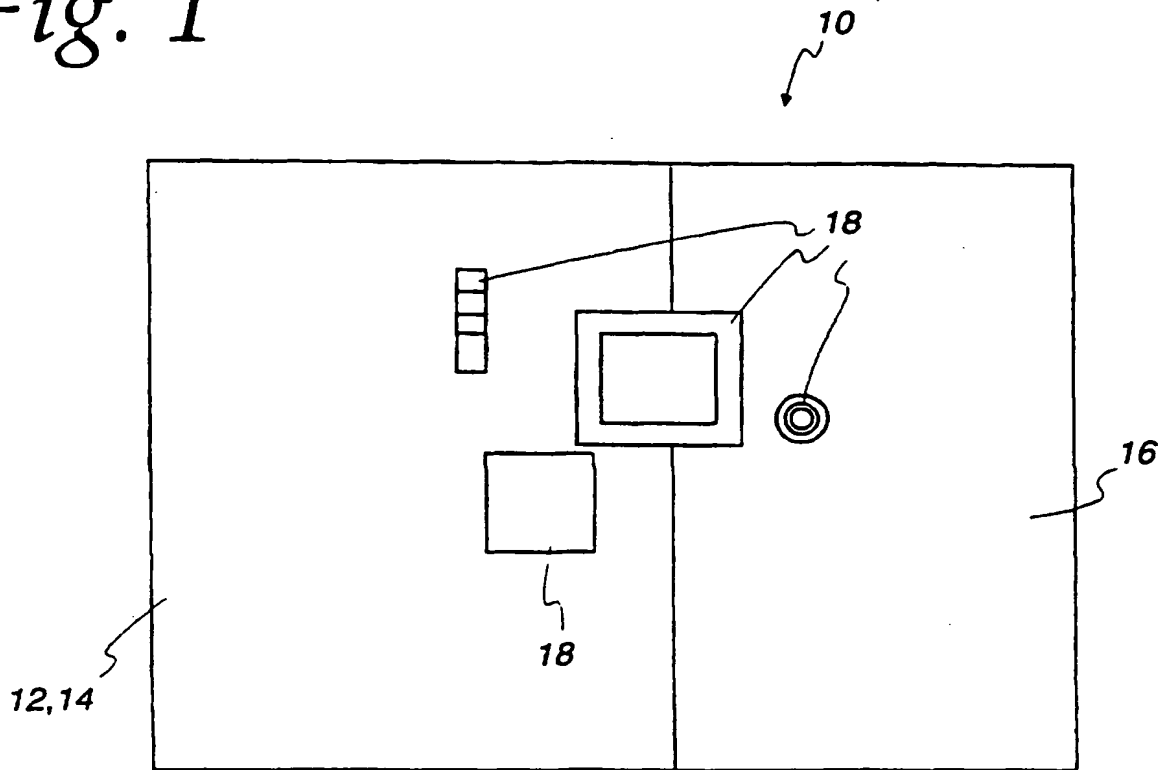
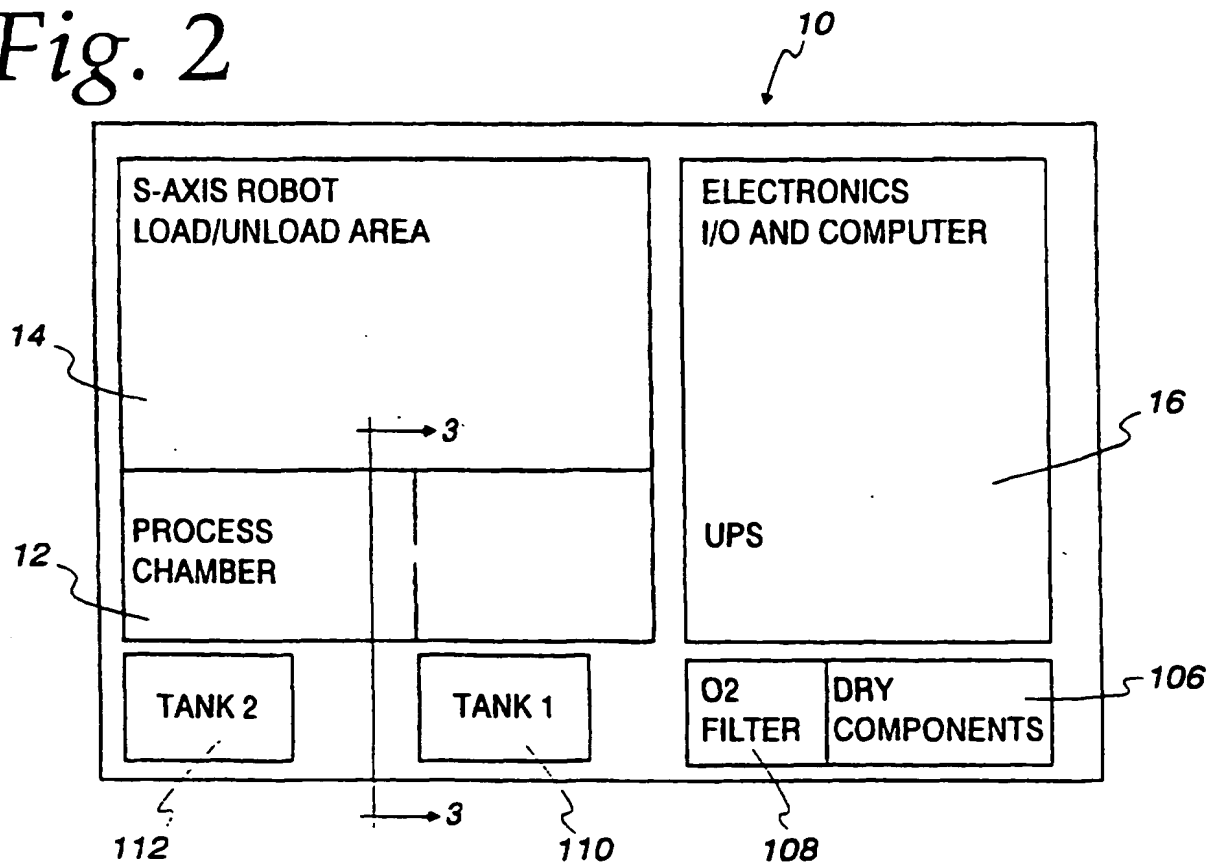
90. The method according to claim 89 wherein the step of providing a carrier fluid comprises the step of providing a plurality of carrier fluid components and mixing said carrier fluid components together to form said carrier fluid.

91. The method according to claim 90 wherein the step of controlling the flow of carrier fluid entering said osmotic membrane degasifier comprises the step of individually controlling the carrier fluid components which are mixed together to form said carrier fluid.

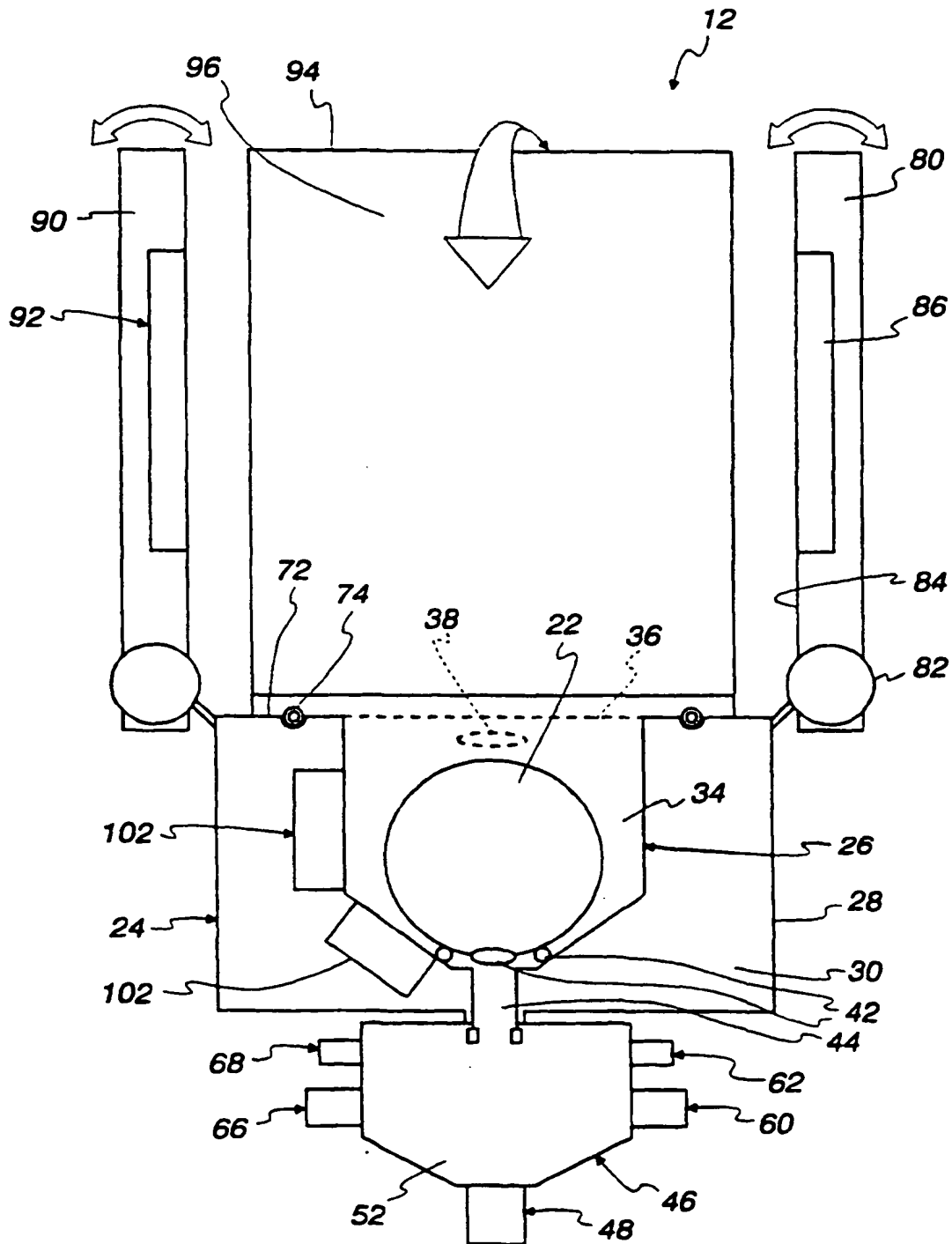
92. The method according to claim 76 wherein said step of contacting the workpiece with said aqueous solution from said osmotic membrane degasifier comprises immersing the workpiece in said aqueous solution.

93. The method according to claim 76 wherein said step of contacting the workpiece with said aqueous solution from said osmotic membrane degasifier comprises spraying the workpiece with said aqueous solution.

94. The method according to claim 76 wherein said step of contacting the workpiece with said aqueous solution from said osmotic membrane degasifier comprises passing said aqueous solution over the workpiece.

*Fig. 1**Fig. 2*



*Fig. 3*

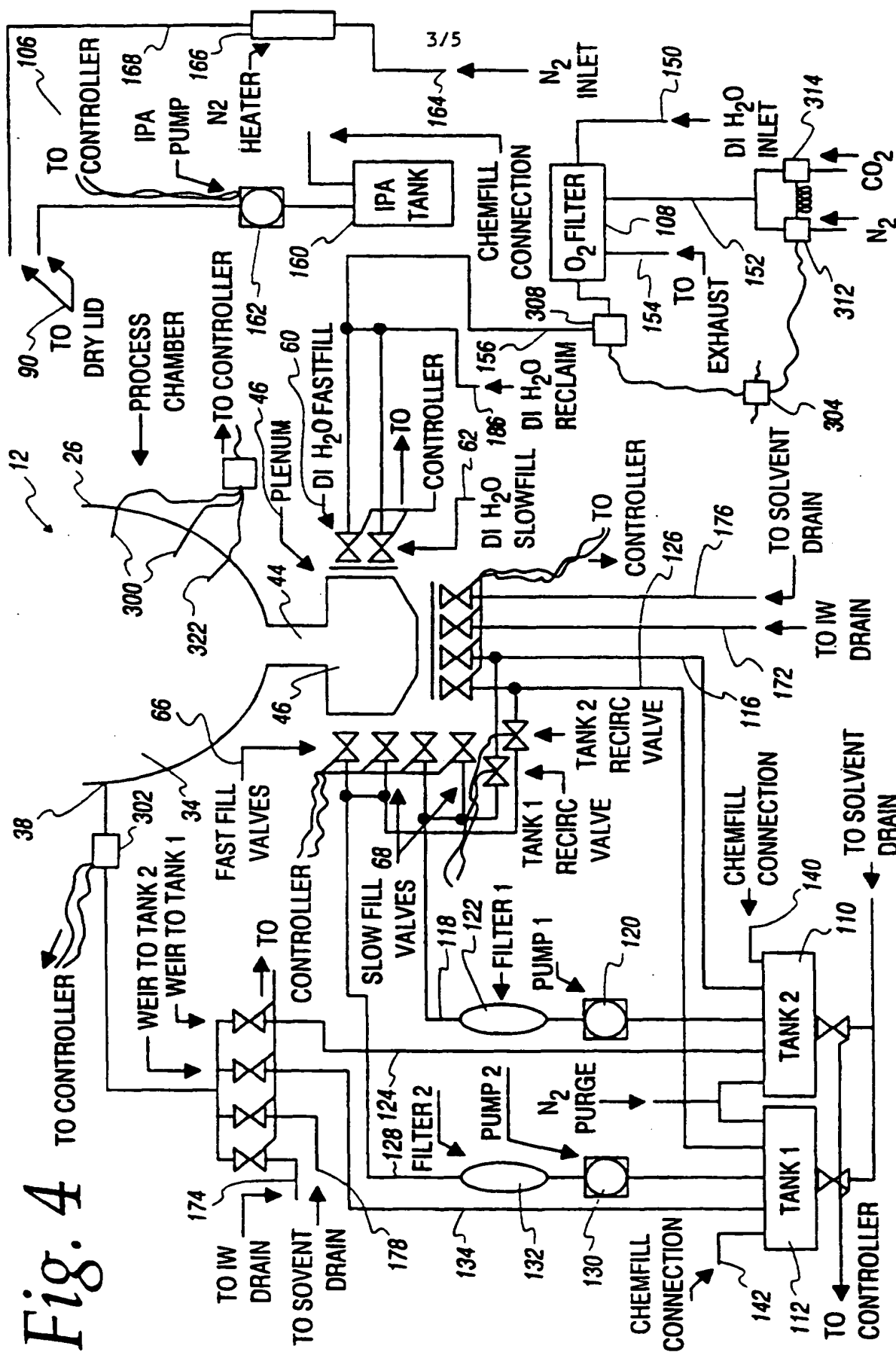
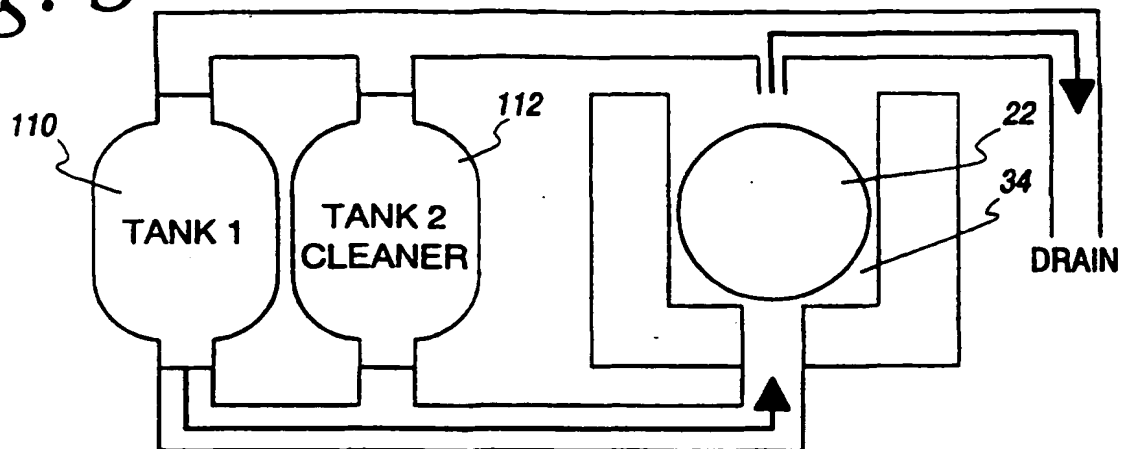
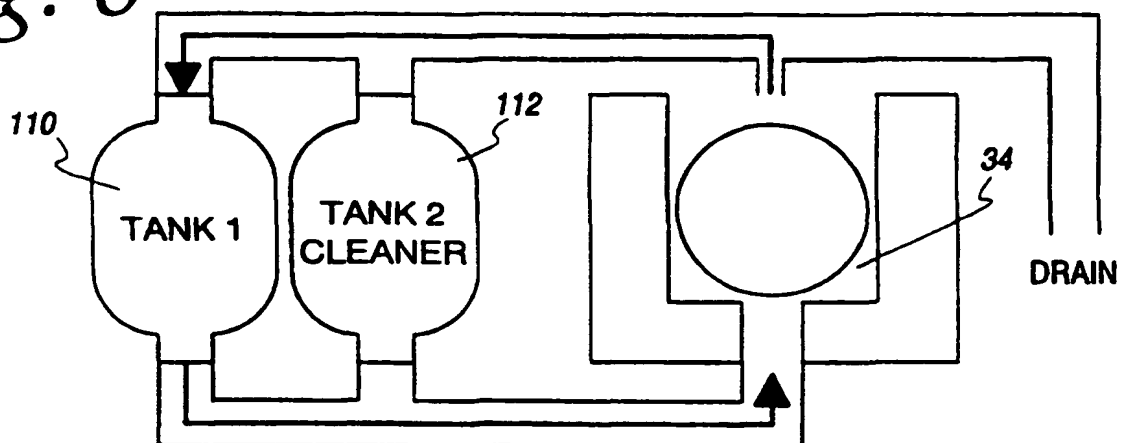
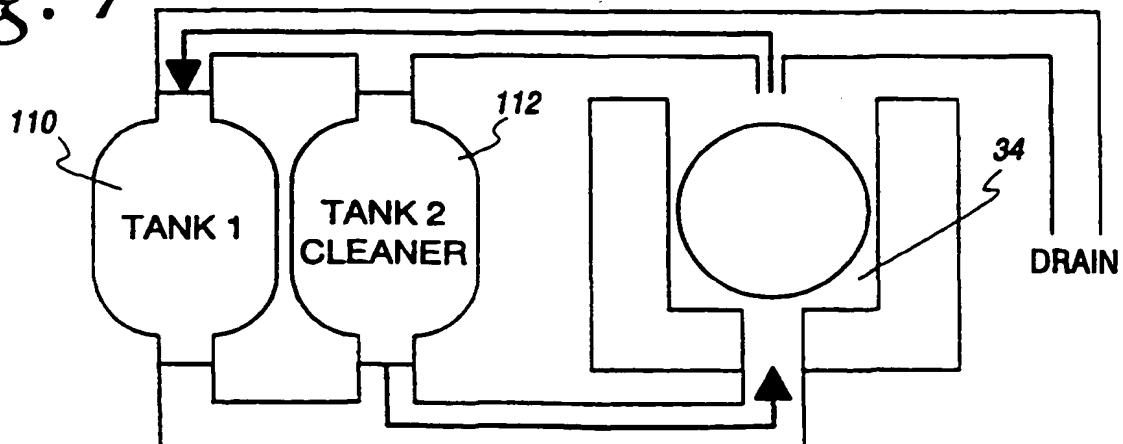


Fig. 4

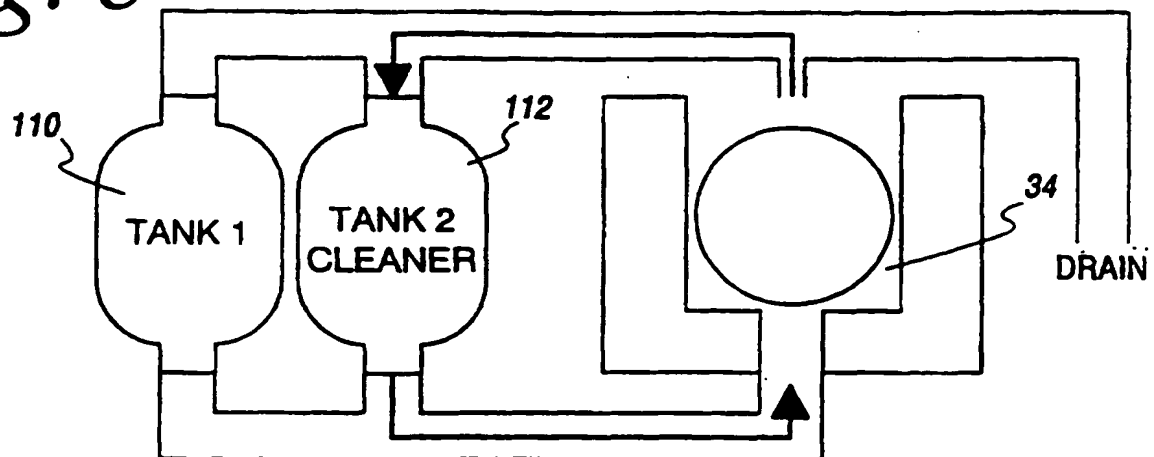
**SUBSTITUTE SHEET (Rule 26)**

4/5

*Fig. 5**Fig. 6**Fig. 7*

*Fig. 8*

5/5



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/11095**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B08B 3/10

US CL :134/1.3

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 134/1.3, 10, 25.4, 94.1, 100.1, 102.1, 110, 111, 184, 200, 902; 210/150, 151, 321.72, 321.75, 321.84

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,990,260 A (PISANI) 05 February 1991.	1-94
A	US 5,518,624 A (FILSON ET AL.) 21 May 1996.	1-94
A	US 5,651,894 A (BOYCE ET AL.) 29 July 1997.	1-94
A	US 5,695,545 A (CHO ET AL.) 09 December 1997.	1-94
A,P	US 5,800,626 A (COHEN ET AL.) 01 September 1998.	1-94
A,P	US 5,833,846 A (TANABE ET AL.) 10 November 1998.	1-94
A,E	US 5,938,922 A (FULK, JR. ET AL.) 17 August 1999.	1-94

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

20 AUGUST 1999

Date of mailing of the international search report

21 SEP 1999

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

FRANKIE L. STINSON  
Telephone No. (703) 308-0661

**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US99/11095**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 3-30329 A (WASHITANI) 08 February 1991.	1-94
A	JP 3-44927 A (KANEDAKI) 26 February 1991.	1-94
A	JP 3-191523 A (YAMAMURA) 21 August 1991.	1-94
A	US 5,409,613 A (WEAVER) 25 April 1995.	1-94

Form PCT/ISA/210 (continuation of second sheet)(July 1992)\*

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/11095

### BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-21 and 62-75, drawn to an apparatus for processing a workpiece.

Group II, claim(s) 22-44, drawn to a method of treating a workpiece.

Group III, claim(s) 45-61 and 76-94, drawn to a method of treating a semiconductor device.

The inventions listed as Groups I-IV do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The special technical feature of Group I is an osmotic membrane having two parts, a first part to direct aqueous solution into contact with one side of the membrane and a second part to direct carrier fluid into contact with the other side of the membrane. The special technical feature of Group II is an osmotic membrane degasifier having a membrane which draws oxygen from the aqueous solution through the membrane to a carrier fluid. The special technical feature of Group III is a method of treating a semiconductor device. Because the special technical feature of the Group I invention is not present in the Group II or Group III claims and because the special technical feature of the Group II claims is not present in the Group I or Group III claims and because the special technical feature of the Group III claims is not present in the Group I or Group II claims, unity of invention is lacking.

Because applicants paid for additional search fees, the ISR is established for claims 1-94.

# PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

## RECEIVED PCT

To:

ELI LILLY AND COMPANY  
Attn. TITUS, Robert-D. *PCT*  
Lilly Corporate Center  
Indianapolis, Indiana 46285  
UNITED STATES OF AMERICA

NOTIFICATION OF TRANSMITTAL OF  
JAN 19 2001 INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

ELI LILLY & COMPANY  
PATENT DIVISION

(PCT Rule 44.1)

*17 JAN 2001*

Date of mailing  
(day/month/year)

17/01/2001

Applicant's or agent's file reference

X-12591

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/US 00/17864

International filing date  
(day/month/year)

21/07/2000

Applicant

ELI LILLY AND COMPANY et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 18:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Further action(s): The applicant is reminded of the following:

Shortly after 18 months from the priority date, the International application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the International application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for International publication.

Within 18 months from the priority date, a demand for International preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 18 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 6818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3018

Authorized officer

John De Bruijn



## NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

### INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

#### What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

#### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

#### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been filed, see below.

#### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

#### What documents must/ may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

## NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 18, 19 and 20; new claims 21 and 22 added."

### "Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

### Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

### Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/selected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/selected Office, see Volume II of the PCT Applicant's Guide.

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>X-12591</b>	<b>FOR FURTHER ACTION</b> <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. <b>PCT/US 00/17864</b>	International filing date (day/month/year) <b>21/07/2000</b>	(Earliest) Priority Date (day/month/year) <b>29/07/1999</b>
Applicant <b>ELI LILLY AND COMPANY et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☒ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No. \_\_\_\_\_

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/17864

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D409/04 A61K31/4535 A61P25/24 A61P3/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D A61K A61P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 436 246 A (RONALD C. BERNOTAS) 25 July 1995 (1995-07-25) the whole document	1-6 ✓
Y	PATENT ABSTRACTS OF JAPAN vol. 016, no. 071 (C-0913), 21 February 1992 (1992-02-21) & JP 03 264583 A (DAI ICHI SEIYAKU CO LTD), 25 November 1991 (1991-11-25) abstract	1-6
Y	EP 0 535 722 A (DUPHAR INTERNATIONAL RESEARCH B.V.) 7 Apr 11 1993 (1993-04-07) the whole document	1-6 ✓
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"B" document member of the same patent family

Date of the actual completion of the international search

9 January 2001

Date of mailing of the international search report

17/01/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5618 Patentkan 2  
NL - 2260 HV Rijswijk  
Tel (+31-70) 340-2040, Tx 31 651 epo nl  
Fax (+31-70) 340-3018

Authorized officer

Beslier, L

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/17864

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 398 413 A (DUPHAR INTERNATIONAL RESEARCH B.V.) 22 November 1990 (1990-11-22) the whole document	1-6 ✓
P,Y	EP 0 982 304 A (ELI LILLY AND CO.) 1 March 2000 (2000-03-01) the whole document	1-6 ✓
P,Y	WO 00 00196 A (ELI LILLY AND CO.) 6 January 2000 (2000-01-06) the whole document	1-6 ✓
P,Y	WO 00 00303 A (ELI LILLY AND CO.) 6 January 2000 (2000-01-06) the whole document	1-6 ✓

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 00/17864

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:  
Although claims 3-6 are directed to a method of treatment of the human/animal body, the search has been carried out and based on the alleged effects of the compound/composition.
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/17864

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5436246 A	25-07-1995	AT 162190 T	15-01-1998
		AU 671494 B	29-08-1996
		AU 5132193 A	12-04-1994
		CA 2144947 A	31-03-1994
		DE 69316377 D	19-02-1998
		DE 69316377 T	27-08-1998
		EP 0660832 A	05-07-1995
		ES 2112434 T	01-04-1998
		FI 951249 A	16-03-1995
		GR 3026297 T	30-06-1998
		HU 72662 A	28-05-1996
		JP 8501559 T	20-02-1996
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		NO 951015 A	15-05-1995
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		WO 9406789 A	31-03-1994
		DK 660832 T	14-09-1998
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EP 535722 A	07-04-1993	AU 648185 B	14-04-1994
		AU 1955492 A	21-01-1993
		CA 2073643 A	16-01-1993
		CN 1070644 A, B	07-04-1993
		CZ 9202168 A	17-02-1993
		FI 923201 A	16-01-1993
		HU 62887 A	28-06-1993
		JP 5213943 A	24-08-1993
		NO 922732 A	18-01-1993
		NZ 243516 A	27-04-1994
		US 5409940 A	25-04-1995
		ZA 9205184 A	28-04-1993
EP 398413 A	22-11-1990	AU 625664 B	16-07-1992
		AU 5494490 A	22-11-1990
		CA 2016625 A	16-11-1990
		JP 3017058 A	25-01-1991
		NZ 233645 A	25-06-1992
		US 5296497 A	22-03-1994
		ZA 9003626 A	27-02-1991
EP 982304 A	01-03-2000	AU 4726699 A	17-01-2000
		WO 0000198 A	06-01-2000
WO 0000196 A	06-01-2000	AU 4850199 A	17-01-2000
WO 0000303 A	06-01-2000	US 6021791 A	08-02-2000
		DE 19928572 A	13-01-2000
		GB 2339071 A	12-01-2000
		US 6146468 A	14-11-2000